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Material Research

by

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Introduction

Previous studies[1-6] have shown that the amount of undercooling in liquid immiscible metals is determined by the relative volume fraction of the components and, in particular, the minority phase's wettability and separation at the container/sample interface. Several theories[7,8] have predicted an asymmetry about the critical composition (C_c) in the wetting versus composition diagram and in the amount of undercooling. However, the degree of undercooling predicted from theory varies significantly from that minuscule amount of available experimental data. There has been only one reported investigation of low-gravity AND true containerless solidification of metal immiscibles.[9] This study showed promising results for attaining a dispersed morphology of minority phase droplets and some undercooling.

The primary objective of this work is to determine if processing immiscible metals in a containerless environment will alter the surface wetting mechanism and the extent to which this will lead to changes in the subsequent nucleation kinetics. The 105-meter Drop Tube Facility at Marshall Space Flight Center provides a low-gravity, containerless, and quiescent environment for this study.[10] Several metal systems will be discussed here that have been initially examined after processing in the Drop Tube.

Experimental Method

In the belljar atop the Drop Tube, the samples were melted in a levitation coil powered by a 10 kW Lepel generator. Temperatures in the belljar were measured with an Ircon Modline 2-color pyrometer. Six-nines pure argon or helium gas was used for forced-convective cooling or to prevent the coil from arcing in a vacuum when the sample was too vaporous. The incandescence of the falling drops was monitored with Si photodiodes spaced every 7.4 meters along the Drop Tube's length and with a time-marked CCD camera. Recalescence could then be determined as a function of free-fall time from which calculated undercoolings can be obtained. Post-processing analysis was performed with a Hitachi Model S4100 field emission scanning electron microscope (SEM) with energy dispersive spectroscopy (EDS) capability.

All starting materials were made from bulk supplies of at least 3-nines purity. The vanadium had to be etched to remove an oxide layer. All materials were then arc-melted into alloy pellets about 5mm diameter. As expected, all arc-melted samples showed a distinct separation of the two constituents which prompted little analysis at this time.

Preliminary Results

Several systems of immiscible metals were selected for initial study, one of which was Sn-Cr(59w/o). The phase diagram can be found in Figure 1a. When samples of these

materials were melted in a gas atmosphere, significant vaporization occurred creating a plume which sometimes blocked the pyrometer view; or, if processed in a vacuum, arcing of the levitation coil occurred. Additionally, the sample did not remain stable within the coil as it was being heated through the liquid-liquid region of the miscibility dome: the samples either sheared themselves apart from uncontrolled spinning or fell out of the coil with a large horizontal velocity component which made them hit the Tube walls. However, several samples were controlled and heated above the critical consolute temperature (T_c ~1485°C) before release. One sample reached 1690°C before losing its levitability and falling out of the coil. For this sample, recalescence was observed after ~1.5 second of free-fall.

Internal examination of this spherical sample made by the SEM indicated an overall chemical composition of 66 w/o Sn. From the original composition, this indicates a significant loss of Cr had occurred in the arc-melting and/or the Drop Tube processing. This composition was still well within the immiscibility dome range (40-74 w/o Sn) and just slightly hyper-critical (C_c ~62 w/o Sn). Figure 2 is the SEM photograph of the microstructure showing a uniform distribution of dendritic clusters. The dendrites are composed of 97 w/o Cr (α-phase) resting in a 2-nines pure Sn matrix, as predicted by the equilibrium phase diagram. Solidification must not have been rapid enough to cause any extension of the solubility of the α-phase.

Samples of Ti-Ce(74 w/o) composition, were also processed. The Ti-Ce phase diagram can also be found in Figure 1b. Due to cerium's extremely small equilibrium oxygen partial pressure(less than 10^{-30} atmospheres at 1000°K), great care was taken in sample preparation. Flowing argon in a glovebox was used for cutting and weighing the materials, and the cerium and alloys were stored under ethanol. These samples were then processed in a 630 Torr He atmosphere resulting in very little vaporization. However, most of the samples that were retrieved from the Tube had a yellowish tint on the surface indicating oxidation.

One sample that was released at a temperature of about 260 degrees above T_c (~1660°C) appeared to have recalesced about 1.7 seconds into free-fall. Figure 3 shows the internal morphology of this sample. The constituents have almost completely separated into the concentric sphere configuration. The inner large sphere consist of Ti(78 w/o) and the smaller satellite spheres of Ti(82 w/o). The outer shell is 3-nines pure Ce. A noticeable separation exists between the outer shell and inner sphere indicating a lack of wetting at the interface between the two phases. Since the Ti coalesced and solidified before the Ce solidified, the temperature would have dropped from the release temperature of 1920°C to the monotectic temperature of 1450°C within the first two seconds of free-fall.

Oxygen analysis of the Ti-Ce materials was performed by Leco Corporation and is presented in Table 1. The Drop Tube samples had 1000 ppm more of oxygen than the sum of that found in the original constituents but less than that found in the samples which had only undergone the arc-melting process. This might be attributable to the

amount of Ce surface area exposed from severely separated arc-melted samples versus the Drop Tube sample.

Table 1. Oxygen Concentration, ppm, in 99.99% Ce and 99.99+% Ti.

	Manufacturer's Specifications	LECO Analyzed		
	Pure	Pure	Arc-Melted Alloy	Drop Tube Alloy
Ce	NA	690	6700	2860
Ti	400	1170		

Future Plans

Of those materials initially studied in this work it was found that the levitation coils and processing conditions need to be optimized to attain more stable levitation and good pyrometry. This is a known problem when trying to overheat liquid metals in levitation coils which lowers the viscosity and causes instability. If stable levitation can be accomplished, then it has been shown that quantifiable undercooling can be observed. If the following cannot be achieved, then other furnace capabilities such as a dripper furnace may be needed to eliminate the vapor loss and allow stable heating through the immiscible dome of systems yet to be attempted.

From the initial research presented herein, it has been shown that the objectives of this research should be attainable. The objectives of this research may also be reached in a less-arduous manner by performing low-temperature experiments in other facilities. These experiments could be performed in most levitation devices (one-g). However, for the low-g experiments the longer cooling times needed for lower temperatures may rule out the use of all microgravity facilities except the long-duration capability of the Shuttle. A low temperature apparatus such as the Microgravity Electromagnetic Levitation (MEL) system or the Electrostatic Levitator would provide direct and distance-invariant optical observation of the drop and its temperature. Also, since heating and levitation are independently controlled, this would provide heating the liquid-liquid immiscible through the miscibility dome while independently eliminating the destructive spinning or oscillations that occur in other levitation systems.

References

1. Gelles S. H. and Markworth A. J., 15th AIAA Conf., Los Angeles 1977, paper 77-122.
2. Potard C., 17th AIAA Conf., New Orleans 1979, paper 79-0173.
3. Ahlborn, H., Lohberg, K., 17th AIAA Conf., New Orleans 1979, paper 79-0172.

4. Perepezko J. H., Galup C., Cooper K.P., in **Materials Processing in the Reduced Gravity Environment of Space** (Guy Rindone, ed., Elsevier Science Pub. Co., Amsterdam, 1982), p. 491.
5. Uebber N. and Ratke L., Scripta Mettall., 25, 1133(1991).
6. Granasy L. And Ratke, L., Scripta Mettall., 28, 1329(1993).
7. Cahn J. W., J. Chem. Phys., 66(8), 3667(1977).
8. Teletzke G. E., Scriven L. E., Davis T. H., J. Colloid Interface Sci., 87(2), 550(1982).
9. Andrews J. B., Briggs C. J., Robinson M. B., in Proc. 7th European Symposium on **Materials and Fluid Sciences in Microgravity** (Oxford, UK, ESA SP-295, 1989), 121.
10. Rathz, T.J., Robinson, M.B., Hofmeister, W.H., Bayuzick,R.J.,"The Marshall Space Flight Center Drop Tube Facility", Rev. Sci. Instrum.,61(12), 3846 (1990).

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16. Abstract

Containerless processing experiments in space and in ground-based facilities such as the Drop Tube Facility at Marshall Space Flight Center provide a unique capabilty to study materials processing phenomena without the influence of walls on nucleation processes. This research will further develop that capability by new experiments with immesible systems. Nucleation and undercooling phenomena will be monitored using infra-red temperature measurements.

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